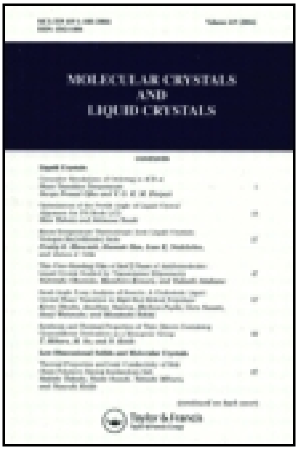

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Liquid Crystallinity in Relation to Composition and Temperature in Amphiphilic Systems

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Liquid Crystallinity in Relation to Composition and Temperature in Amphiphilic Systems†

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Abstract—The purpose of this paper is to give a broad review of the " fused " type of liquid crystalline phases formed by amphiphilic compounds and to examine the constitutional relationships of these phases to one another and to the amorphous liquid phase. Further, an account will be given of how, on changes in composition and temperature, the various phases undergo reversible interconversions through first-order phase transitions. It will be shown how these transitions follow a regular pattern which, qualitatively, can be satisfactorily interpreted on a molecular basis.

Distinction between Semicrystalline and Fused Mesophases

The fused liquid crystalline phases to be considered are formed by amphiphilic compounds either in the pure state or, more generally, in binary or multicomponent solutions. Before they are discussed the restriction in scope expressed in the term " fused " will be examined.

Among the most comprehensively studied of amphiphilic compounds are the sodium soaps. At room temperature the sodium soaps from lamellar crystals of the character indicated diagrammatically in Fig. 1. Both the hydrocarbon groups and the polar groups are arranged in regular three-dimensional solid-crystalline order. When the sodium soaps are heated they undergo a regular series of first-order phase transitions before the amorphous liquid melt is finally produced. It has been shown by Luzzati and associates$^{(1)}$ by X-ray

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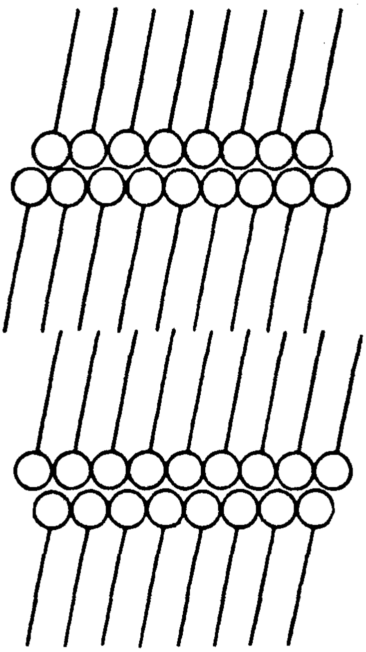


Figure 1. Character of solid lamellar soap crystal. Both the hydrocarbon groups and the polar groups are arranged in regular three-dimensional solid crystalline order.

diffraction studies that this behaviour arises because the three-dimensional crystalline organization of the hydrocarbon groups breaks down at a temperature a little above 100 °C, while the crystalline arrangement of the polar groups persists, in some measure, up to considerably higher temperatures. With rising temperature, however, this crystalline order breaks down in a series of steps at definite transition points that are characteristic for each soap, and thus gives rise to a succession of mesophases which are both partly crystalline and partly liquid in character. Such semicrystalline mesophases will not be further considered in this discussion.

At a temperature in the region of 300 °C, depending on the particular sodium soap, the crystalline arrangement of the polar groups is finally lost, but even then the amorphous liquid phase is not at first produced. It is preceded by a smectic (Greek, smegma–soap) mesophase or liquid crystal whose structure will shortly be considered. This " fused " mesophase undergoes a first-order phase transition

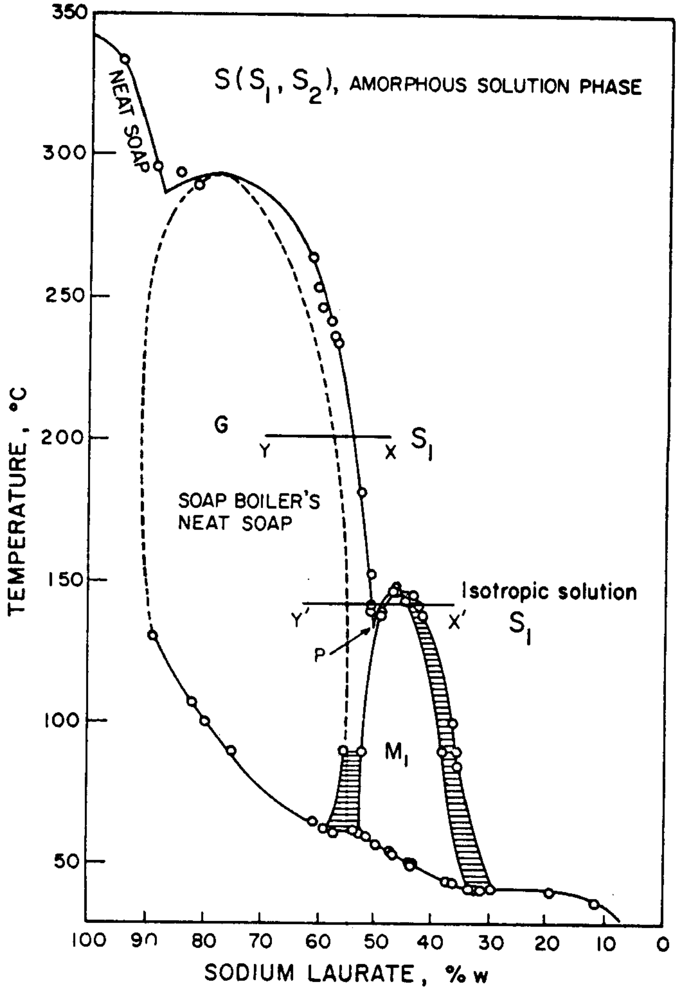


Figure 2. Phase diagram for the sodium laurate/water system showing homogeneous fields of each of the different solution phases and isothermal tie lines connecting the phases in heterogeneous equilibria.(5)

to the amorphous melt at a somewhat higher temperature (cf. Fig. 2).

It should be remarked here that, at lower temperatures under certain conditions, semicrystalline soap mesophases arise in which, while the hydrocarbon groups retain crystalline order, the polar groups have been brought into the " labile " or fused condition through the solvent action of water. This situation, according to

Vincent and Skoulios(2) is found in the lamellar " gel " phases formed at room temperatures by, for example, potassium or rubidium stearates in the presence of water. This second class of semicrystalline mesophase is again outside the scope of this paper.

Fused Mesophases

The present paper is thus concerned only with the amorphous liquid phase (pure melt or solution) and with those mesophases in which both the hydrocarbon and polar zones are in the " fused " or " labile " state.

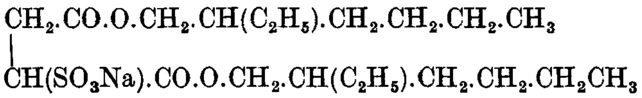
Amphiphilic compounds, depending on their constitution, form a number of individually distinct types of fused mesophase. Further, depending on temperature and the presence of additional components, a particular amphiphile may give rise to several types of mesophase. Each type is constructed according to a definite structural pattern which confers on it clearly defined diagnostic features of behaviour such as optical properties,(3) X-ray diffraction spectra,(1) N.M.R. spectra(4) etc. The individual types of mesophase and their interconversions under the influence of changes in composition and temperature will now be considered, with the help of some specific examples.

THE LAMELLAR MESOPHASE G: " NEAT " PHASE

Figure 2(5) illustrates the ranges of stability of the " fused " phases in the sodium laurate/water system. These phases are the amorphous liquid phase, the " neat soap " phase, the " soap boiler's neat soap " phase and the " middle " phase. The last three are birefringent liquid crystalline phases. The structure of the " neat soap " phase consists essentially of a succession of planar liquid monolayers of soap molecules.(1) These monolayers are arranged alternately so that, as in the solid crystal, like is juxtaposed to like. The juxtaposed hydrocarbon chains constitute a layer of the character of a fused hydrocarbon while the juxtaposed polar groups have the character of a fused salt. Limited amounts of additional hydrocarbon may be incorporated into the hydrocarbon layer and limited amounts of water may be incorporated into the polar zone before any phase change occurs. Incorporation of hydrocarbon will be referred to later in this article and the discussion at the present stage will be restricted to binary aqueous systems.

The neat soap phase is able to incorporate only a small amount of water before undergoing a phase transition which, depending on temperature (Fig. 2), leads to the formation either of the amorphous solution phase or of the " soap boiler's neat " phase. The transition to this second, more aqueous, lamellar phase probably involves a change in the mutual orientation of the polar groups within the individual monolayers. This point will be considered further later.

The second, more aqueous, lamellar liquid crystalline solution phase is stable over a wide range of composition and temperature. This type of aqueous lamellar mesophase is formed in many other binary amphiphile/water systems, as for example with Aerosol OT



$$\begin{array}{l} \mathrm{CH_2.CO.O.CH_2.CH(C_2H_5).CH_2.CH_2.CH_2.CH_3} \\ | \\ \mathrm{CH(SO_3Na).CO.O.CH_2.CH(C_2H_5).CH_2.CH_2.CH_2CH_3} \end{array}$$

(Fig. 3),(6) *N*,*N*,*N*-trimethylaminododecanomide (Fig. 4),(7) dodecyltrimethylammoniumchloride (Fig. 5),(8) as well as in many ternary and multicomponent systems.(9,10,11) In the speaker's system of nomenclature it was termed the *G* phase on account of its usually rather thin gel-like consistency. Other nomenclatures have also been used, for example, neat phase, phase *D* (Ekwall and associates) and phase *LL* (lamellar labile, Luzzati and associates).

The fact, established by X-ray and optical studies, that in the *G* phase the amphiphilic monolayer $\bar{C}$ remains statistically planar, except where subject to mechanical deformation, shows that in this phase, whose structure is represented diagrammatically in Fig. 6, the tendencies of the $\bar{C}$ monolayer to become convex towards its lipophilic environment, $\bar{O}$, on the one hand and towards its polar environment, $\bar{W}$, (usually aqueous) on the other, are equally balanced. Barred symbols are used here to indicate (i) that $\bar{C}$ may be a mixed monolayer containing several amphiphilic species; (ii) that the lipophilic region $\bar{O}$, which in the simplest case contains the liquid juxtaposed hydrocarbon groups of two $\bar{C}$ monolayers, may also contain in solution, besides a fraction of the amphiphile, added hydrocarbon-soluble additives, such as hydrocarbons or halohydrocarbons; and finally (iii) that the $\bar{W}$ region, which in the

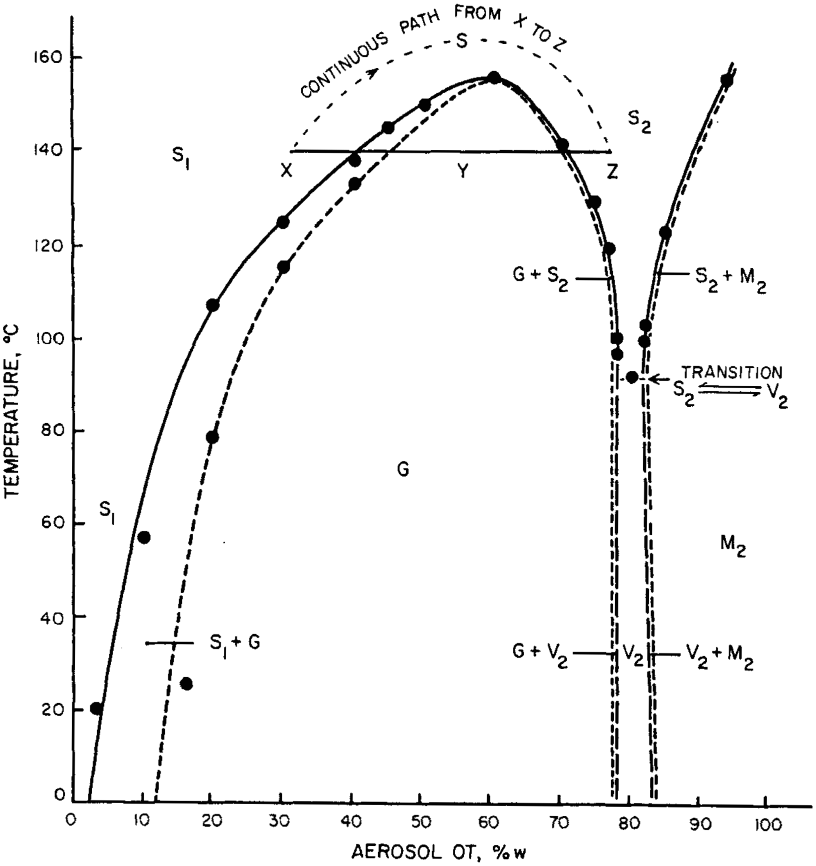


Figure 3. Phase diagram for the Aerosol OT/water system.(6) The boundaries indicated by broken lines are tentative.
$S(S_1, S_2)$ = Mobile isotropic phase; G = Neat phase;
M_2 = Inverse middle phase; V_2 = Inverse viscous isotropic phase

simplest case contains the fused juxtaposed polar groups of two $\bar{C}$ monolayers, more usually contains water which may contain in solution, besides a fraction of the amphiphile present (Fig. 6), such water-soluble additives as inorganic salts, sugars, the lower organic hydroxy compounds etc.

If we define a ratio $R^{(10,11)}$ as

$$\frac{\text{tendency of } \bar{C} \text{ layer to become convex towards } \bar{O}}{\text{tendency of } \bar{C} \text{ layer to become convex towards } \bar{W}},$$

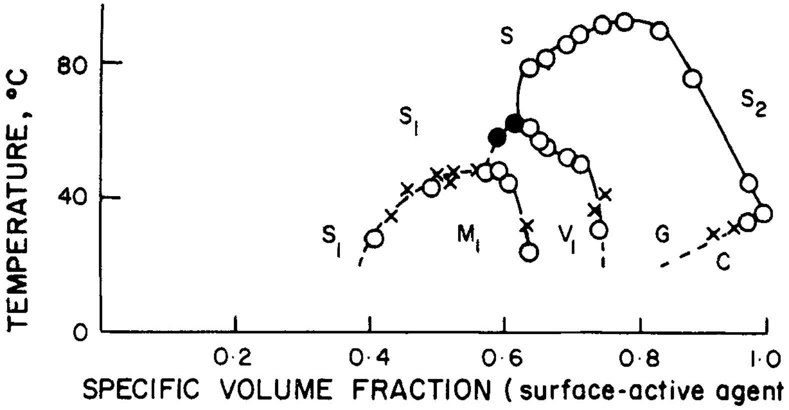


Figure 4. Phase diagram for the N,N,N-trimethylaminododecanoimide/water system.(7) Phase boundaries were determined from optical ○, density x and X-ray diffraction ● measurements. $S(S_1, S_2)$, mobile isotropic solution (amorphous solution). M_1, middle phase; V_1, viscous isotropic phase; G, neat phase; C, crystals; the two-phase zones are narrow and are not indicated.

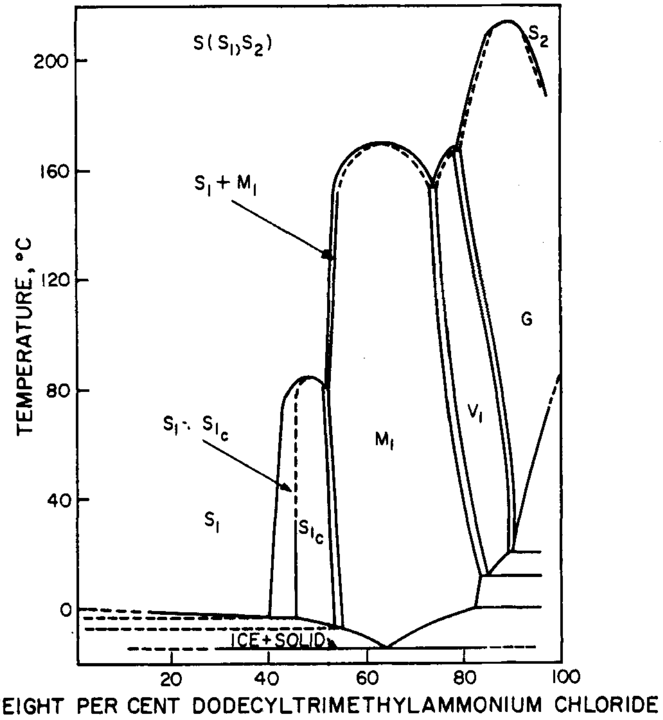


Figure 5. Phase diagram for the dodecyltrimethylammonium chloride/water system.(8) ——, Experimental boundary; – – –, interpolated boundary.

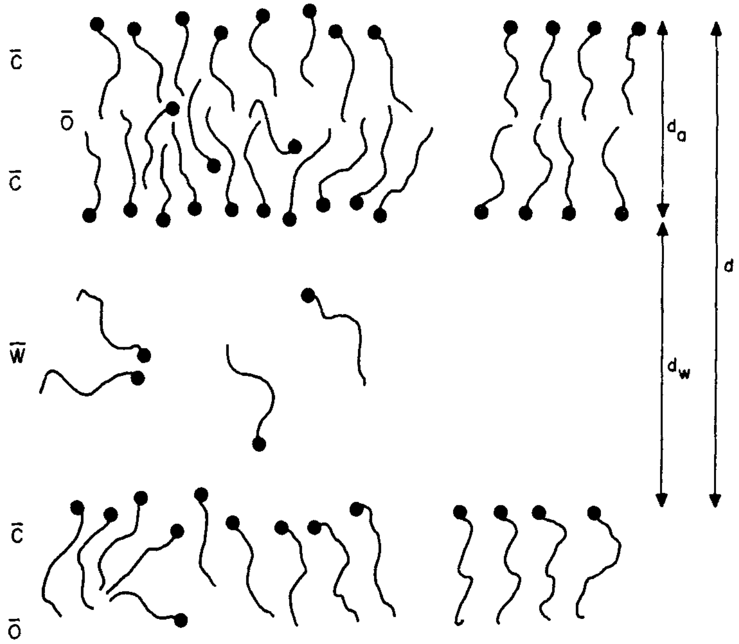


Figure 6. Diagrammatic representation of the structure of the G phase in a binary amphiphile water system. Left, situation in principle: $\bar{C}$ layer contains most of the amphiphile but both amphiphile and water are distributed throughout the $\bar{C}$, $\bar{O}$ and $\bar{W}$ regions so as to maintain their respective activities statistically uniform throughout. Right, working approximation usually employed in X-ray studies: $\bar{C}$ layer contains only and entirely all the amphiphile present.

then within the G phase, since the planar lamellar structure is stable, $R = 1$.

The ratio R will be largely dependent on the ratio

$$\frac{\text{tendency of } \bar{C} \text{ layer to spread out into the } \bar{O} \text{ region}}{\text{tendency of } \bar{C} \text{ layer to spread out into the } \bar{W} \text{ region}}\,.$$

The tendency of the $\bar{C}$ layer to spread out into the $\bar{O}$ region will be promoted by attractive molecular interactions between $\bar{C}$ and $\bar{O}$, $A_{\bar{C}\bar{O}}$, and opposed by attractive interactions (cohesion) within $\bar{O}$ itself, $A_{\bar{O}\bar{O}}$. Similarly, the tendency of the $\bar{C}$ layer to spread out into the $\bar{W}$ region will be promoted by a factor $A_{\bar{C}\bar{W}}$ and opposed by a factor $A_{\bar{W}\bar{W}}$. Thus we may say that R will increase with increase in the ratio

$$\frac{A_{\bar{C}\bar{O}} - A_{\bar{O}\bar{O}}}{A_{\bar{C}\bar{W}} - A_{\bar{W}\bar{W}}}$$

where $A_{\bar{C}\bar{O}}$ etc. are energies of interaction per unit area of interface at the $\bar{C}$–$\bar{O}$ and $\bar{C}$–$\bar{W}$ interfaces respectively.

Further, for a given $\bar{O}$ and $\bar{W}$, R will increase with increase in the ratio $A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}$. This relationship we will denote by the expression

$$R \rightarrow \frac{A_{\bar{C}\bar{O}}}{A_{\bar{C}\bar{W}}}.$$

The intermolecular attractive forces responsible both for $A_{\bar{C}\bar{O}}$ and for $A_{\bar{C}\bar{W}}$ will be partly electrokinetic (forces of lipophilic character, A_L) and partly electrostatic (forces of hydrophilic character, A_H).

The effects of changes in composition and temperature on the ratio R, and consequently on micellar shape, may therefore be considered from the point of view of their probable effects on

$$\left[\frac{A_{\bar{C}\bar{O}}}{A_{\bar{C}\bar{W}}}\right]$$

or more explicitly, on

$$\left[\frac{A_{L\bar{C}\bar{O}} + A_{H\bar{C}\bar{O}}}{A_{L\bar{C}\bar{W}} + A_{H\bar{C}\bar{W}}}\right]$$

In many systems, of which the sodium laurate/water and the Aerosol OT/water systems may be taken as specific examples, the G phase is stable over a wide range of temperature and composition. Over this range the form of the $\bar{C}$ monolayer remains statistically planar ($R = 1$), although thermal fluctuations will give rise to small local distortions ($R > 1$ or $R < 1$) (Fig. 6). Just why the lamellar structure and a statistically unit value of R are maintained over a wide range of compositions and temperatures is not obvious. However, the mechanism by which this is effected is fairly clear, mainly from evidence afforded by X-ray diffraction studies.(1)

The repeat distance, d, (Fig. 6) for any particular experimental G phase may usually be determined directly by X-ray diffraction measurements. The dimensions of other features of the G phase may then be calculated from d, the composition of the G phase and the experimentally estimated partial specific volumes of its components, provided one adopts certain working approximations (see right-hand side of Fig. 6).

For binary aqueous G phases the approximations most frequently adopted may be collectively expressed in the assumption that the G phase may be treated as if the double $\bar{C}$ layers are effectively planar and include only and entirely all the amphiphile molecules present.

If one adopts this assumption, whose acceptability cannot here be discussed in detail, one may readily calculate$^{(1)}$

d_a . . . the thickness of the double $\bar{C}$ layer

d_w . . . the thickness of the aqueous layer, and

S . . . the mean area populated by one polar group at the interface or, more shortly, the "area per polar group". Gallot and Skoulios,$^{(12)}$ using this assumption, have calculated from their measurements of d values the changes with concentration in the area per polar group within the G phases formed by the homologous potassium soaps (C_8—C_{22}). It was found that, at constant temperature, the calculated area increases with decreasing concentration and depends only on the concentration, N, when this is expressed as gram molecules of soap per litre of water (Fig. 7). This result implies that, at constant temperature, the unique area per polar group which at a given value of N leads to unit value of R, is insensitive to the chain length of the soap and consequently to the thickness of the $\bar{O}$ layer.

This suggests that, in the expression $R \rightarrow A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}$ (cf. p. 6), (i) at a given temperature over the range of stability of the G phase (in which $R = 1$), $A_{\bar{C}\bar{O}}$ is not highly sensitive to those changes in the thickness of the $\bar{O}$ layer which necessarily accompany either variation in chain length at a given value of S (corresponding to a given value of N) or variation in S (resulting from variation in N) with a soap of given chain length: (ii) the tendency for increase in $A_{\bar{C}\bar{W}}$, which might be expected to follow increase in water content, is offset by an increase in S, that is by a reduction in the number of polar groups per unit area of interface, which maintains the balance of $A_{\bar{C}\bar{W}}$ with $A_{\bar{C}\bar{O}}$ corresponding to $R = 1$.

For each soap, at a given temperature, there is a minimum thick-

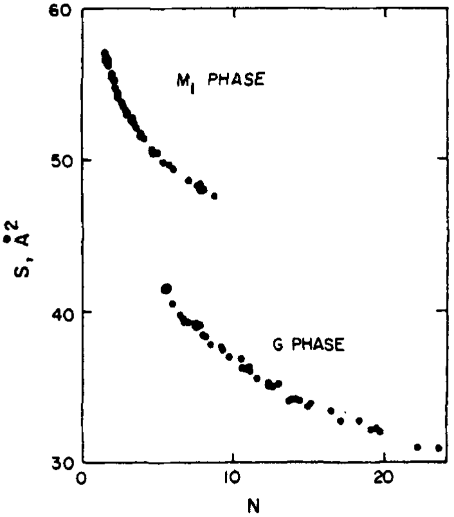


Figure 7. Variation in the area S per polar group with change in concentration N (moles soap/litre water) in M_1 and G solutions of potassium soaps (n-alkanoates) at 86 °C.(12)

ness of the $\bar{O}$ layer (corresponding to a maximum value of S) consistent with the stability of the G phase. At concentrations lower than that at which this minimum thickness is reached, transition to a second phase (either S_1 or M_1 according to the temperature (cf. Fig. 2)) occurs. Since at a given concentration N (with its corresponding unique value of S) the thickness of the $\bar{O}$ layer is approximately proportional to the chain length, it might be expected that the stability of the G phase would extend to lower concentrations with the soaps of higher molecular weight. This behaviour is observed. The points at the left-hand side of the curve for the G phase in Fig. 7 thus correspond to values obtained with soaps of higher molecular weight (up to C_{22}).

The increase in effective area per polar group on dilution probably derives from a decrease in the degree of binding of the counter-ions (K^+) to the micellar surface with increasing water content. Further, a change in the interfacial concentration of the polar groups will be necessary in order to maintain equilibrium with that concentration of the amphiphile (regarded as negligible in the calculations of Gallot and Skoulios) which is actually dissolved in the interlamellar solution

$\overline{W}$ (Fig. 6, left-hand side). That this interlamellar concentration is appreciable, particularly with shorter-chain amphiphilic salts, and that it diminishes with bulk dilution is shown by the colligative properties of amphiphile/water systems. It must be remembered that in these equilibrium systems the activity of each chemical species must necessarily be statistically uniform throughout, although the concentrations within the different zones may differ greatly on account of the large local differences in activity coefficients. Figure 8(13) shows curves of vapour pressure against composition for

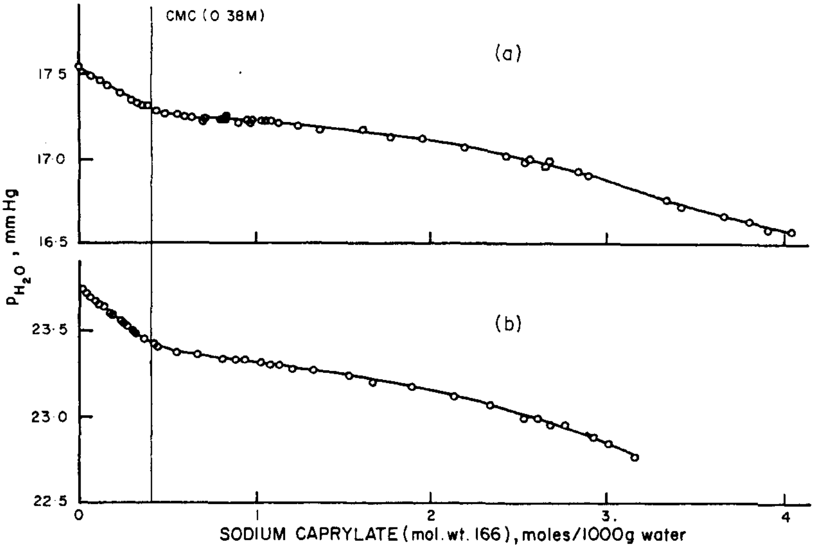


Figure 8. (a) Vapour pressure of sodium caprylate solutions at 20 °C measured by the iso-piestic method. (b) Vapour pressure of sodium caprylate solutions at 25 °C measured by the Mechrolab Osmometer method.(13)

amorphous solutions (S_1) of sodium caprylate. It is clear that in the more concentrated solutions the composition of the $\overline{W}$ region, whose vapour pressure must be equal to that of the system as a whole, cannot approximate to that of pure water. It must, in fact, be of markedly higher concentration (perhaps more than three times) than the critical micelle concentration (cmc about 5%). This conclusion must apply also to the liquid crystalline solutions of sodium caprylate (in this case the M_1 phase which will be considered shortly) formed at still higher concentrations. With the more lipophilic amphiphile, Aerosol OT (cmc about 0.2%), which is however of similar effective chain length, X-ray studies suggest a concentration within the interlamellar solution $\overline{W}$ of the G phase of the order of 5% at 20 °C and of 3% at 83 °C.(14) In the solutions of the higher members of the soaps (C_8—C_{22}) studied by Gallot and Skoulios the interlamellar soap concentrations may, however, well be considerably lower. Where, however, they are still significant, the effect of neglecting them in calculating S values from measured values of d will be to give underestimates of S.(14) The values for S in Fig. 7 may therefore be taken as minimum estimates.

It may be mentioned at this point that for the G solutions of the soaps studied by Gallot and Skoulios and also for the solutions of Aerosol OT studied by Rogers and Winsor, the measured d-spacing diminishes with rise of temperature. The area per polar group, when calculated using the simplifying approximations 1–4 above, correspondingly shows an increase. With the Aerosol OT system, however, when reasonable allowance is made for amphiphile included in the $\overline{W}$ region, this apparent increase in S with rise of temperature largely disappears.(14)

BREAKDOWN OF THE G PHASE ON DILUTION TO GIVE THE AMORPHOUS SOLUTION PHASE S_1

In the sodium laurate/water system (Fig. 2) at temperatures above about 150 °C and in the Aerosol OT/water system at room temperatures, dilution of the G phase beyond its lower concentration limit of stability leads to the separation of a mobile amorphous solution phase S_1. The S_1 phase at first exists in equilibrium with the conjugate G phase, each phase, in accordance with the phase rule, being of fixed composition at a given temperature.

The phase sequence $S_1 \rightarrow (S_1 + G) \rightarrow G$ may be interpreted as follows. Over the range of stability of the G phase, the general tendency of dilution to decrease R, i.e. to favour convexity of the $\bar{C}$ monolayer towards the aqueous region $\overline{W}$, is compensated, as just discussed, by increase in the area per polar group. This compensation process, however, reaches a limit. At this limit the local thermal fluctuations in the form of the C monolayer (Fig. 6), which with progressive dilution increasingly lead to areas convex towards $\overline{W} (R < 1)$, attain a magnitude which causes fragmentation of the lamellae. As would be expected on this view, breakdown occurs sooner, the higher the temperature. At those loci within the lamellar G phase where thermal fluctuations have momentarily produced the highest water content, with consequent lowest momentary value of R, separation of a more dilute aqueous phase S_1 is initiated. This phase is in equilibrium with the residual G phase and therefore, although it is considerably more dilute, shows the same colligative properties (partial vapour pressures, osmotic properties, etc.).

It is this insensitiveness of the osmotic properties to composition which permits those local thermal fluctuations in composition and micellar form within the G phase which, at the limiting dilution, lead to the separation of the relatively more dilute S_1 phase. Complementarily, fluctuations within this conjugate S_1 phase, which is at its upper limit of concentration, lead to separation of the relatively more concentrated G phase. In the S_1 phase, which is thus maintained in equilibrium with the G phase, the form of the $\bar{C}$ monolayer is, on balance, convex towards $\bar{W}(R < 1)$. However, on the fluctuation hypothesis, it would be expected that, locally, lamellar regions would be present within it similar in internal dimensions to those of the G phase itself but of limited extent. X-ray diffraction studies support this view.(15,16) On progressive dilution of the S_1 phase below its upper limit of concentration, i.e. at concentrations at which it is no longer in equilibrium with the G phase, the mean form of the $\bar{C}$ layer tends towards the spherical form, characteristic of the " S_1 " or " Hartley micelles " found at concentrations not too greatly above the cmc.

BREAKDOWN OF THE LAMELLAR MESOPHASE G ON DILUTION TO GIVE THE HEXAGONAL OR " MIDDLE " MESOMORPHOUS SOLUTION PHASE M_1

In the sodium laurate/water system (Fig. 2) at temperatures below 150 °C breakdown of the G phase on dilution does not lead directly to the amorphous solution phase S_1, but a second mesomorphous solution phase, the " middle phase " M_1, is first produced. The essential architecture of this mesophase (Fig. 9) has been definitively established by X-ray diffraction measurements(1) taken in conjunction with optical studies.(17) The amphiphile molecules are, for the most part, aggregated into indefinitely extended parallel

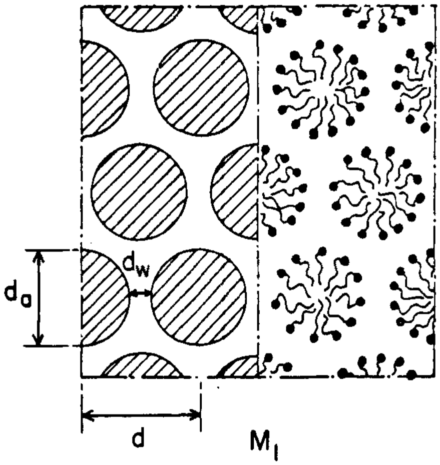


Figure 9. The structure of the middle M_1, phase in relation to the measured X-ray long spacing, d.(1)

cylindrical or fibrous micelles which are ordered in two-dimensional hexagonal array. In the M_1 phase, as in the G phase and all other amphiphilic solution phases, there is a kinetic equilibrium of molecules between the $\bar{C}$, $\bar{W}$ and $\bar{O}$ regions, the activity of each molecular species necessarily being statistically uniform throughout the equilibrium system. However, in X-ray diffraction studies of the M_1 phase the simplifying approximation is usually adopted that the fibrous micelles contain solely and entirely all the amphiphile present as represented in Fig. 9.

In the M_1 phase, except when subject to mechanical constraint, the liquid fibrous micelles maintain their indefinitely extended parallel arrangement. It is therefore clear that, parallel to the fibre axis, $R = 1$, while circumferentially, $R < 1$. This implies that the force fields around the micellized amphiphile molecules do not interact in a statistically symmetrical manner about the long axes of adjacent molecules.

It appears from its solvent behaviour and from X-ray diffraction studies, that the micellar $\bar{O}$ region is essentially of " random liquid " character.(1) The dissymmetry of R in the M_1 phase therefore seems to imply that there is mutual ordering of the polar groups at the $\bar{C}$—$\bar{W}$ interface. At the $\bar{C}$—$\bar{W}$ interface the polar groups in the M_1 phase must therefore be regarded as constituting a two-dimensional liquid crystalline interfacial solution in equilibrium with the $\overline{W}$ region. In relation to the orientation of the polar groups within the $\overline{C}$ layer, we may denote the direction in which R is a minimum by x and the direction in which R is a maximum by y. With this convention, in the M_1 phase, around the micelles $R_x < 1$ while along them $R_y = 1$.

From their X-ray diffraction measurements with the G and M_1 phases formed by the homologous potassium soaps, Gallot and Skoulios⁽¹²⁾ have calculated, using the approximations noted above, the area, S, per polar group in the two phases at various compositions and temperatures (Fig. 7).

In both phases, with increasing dilution, there is a progressive increase in S which, in each phase, is dependent only on N, as already considered above for the G phase. Further, corresponding to the change of phase $G \rightarrow M$, there is a marked increase in S. These calculated increases would be even greater if allowance were made for intermicellar amphiphile within the $\overline{W}$ region.

It seems unlikely that the mutual ordering of the polar groups, indicated in the case of the M_1 phase by the dissymmetry of R, will be lost in the conjugate G phase in which the polar groups are closer together. The fact that, in the G phase, $R = 1$ in all directions must therefore imply that in passing from the M_1 phase ($R_x < 1$; $R_y = 1$) to the G phase on increase in concentration, differential compression of the polar groups in the x and y directions produces the condition in which both $R_x = 1$ and $R_y = 1$. In spite of this, the ordering of the polar groups would be expected to make each individual monolayer optically biaxial. The fact that the G phase is optically uniaxial would then imply that the successive parallel monolayers are stacked at random.

BREAKDOWN OF THE M_1 PHASE ON DILUTION TO GIVE THE S_1 PHASE

The M_1 phase, like the G phase, is stable over a considerable range of compositions. The condition, $R_x < 1$; $R_y = 1$, is maintained with increasing water content by a progressively increasing area per polar group, in a manner analogous to that discussed for the G phase. However, with increasing dilution, thermal fluctuations will increasingly tend to produce local convexities towards $\overline{W}$ along the length of the fibrous micelles. A limiting dilution is ultimately reached at which fragmentation of the micellar fibres and breakdown of the M_1 phase occur at loci where fluctuations have momentarily given rise to a relatively high water content. The amorphous S_1 phase, which is of higher water content than the residual conjugate M_1 phase, separates. This S_1 phase *contains locally regions of* M_1 *structure*,(18) the situation being analogous to that already discussed for the $G \rightarrow (G+S_1)$ sequence. On further dilution and further increase in R the local M_1 regions diminish in significance and the average micellar form approaches the spherical S_1 or Hartley type.(18)

It is of particular interest that Aerosol OT and many other amphiphiles in which the lipophilic moiety is laterally relatively bulky do not yield an M_1 phase on dilution of the G phase. This is presumably because the laterally bulky lipophilic groups prevent sufficiently close mutual approach of the polar groups for the occurrence of the mutual orientation that is required for the formation of the M_1 phase.

BREAKDOWN OF THE G PHASE ON INCREASE IN CONCENTRATION TO GIVE THE AMORPHOUS SOLUTION PHASE S_2

We have already discussed how the general tendency of R to decrease with dilution can lead to the phase sequence,

$$\begin{array}{ccc} G \rightarrow & (G+S_1) & \rightarrow S_1, \\ R=1 & & R<1 \end{array}$$

as indicated in Fig. 2 and Fig. 3 for dilution along the lines marked YX.

In certain circumstances, as indicated in Fig. 3 along the line marked YZ, increase in concentration with consequent increase in R may lead to the complementary sequence

$$\begin{array}{ccc} G \rightarrow & (G+S_2) & \rightarrow S_2. \\ R=1 & & R>1 \end{array}$$

In the amorphous S_2 solution the mean form of the $\bar{C}$ monolayer will be convex towards $\bar{O}$, complementarily to its convexity towards $\bar{W}$ in the S_1 solution. There is, however, usually no uniform micellar form nor long-range order in either the S_1 or S_2 solutions, but rather a thermal equilibrium of fluctuating micellar forms. By following the path indicated by the dotted line in Fig. 3 it is possible to pass continuously from the S_1 solution, X, to the S_2 solution, Z, without encountering any change in phase or any abrupt discontinuity in properties, such as are found in proceeding along the discontinuous path, XYZ. " S_1 " and " S_2 " should therefore be considered as parts of a single solution phase S rather than as distinct individual phases. The designations S_1 and S_2 conveniently distinguish those regions of the S phase in which the mean form of the $\bar{C}$ monolayer predominantly tends to convexity towards $\bar{W}$ and to convexity towards $\bar{O}$ respectively.

FORMATION OF THE " INVERSE MIDDLE MESOPHASE " M_2

An " inverse middle " phase, M_2, complementary in character to the M_1 phase is found in the Aerosol OT/water system (Fig. 3) at concentrations somewhat higher than the upper limit of concentration for the G phase. The M_2 phase is also found in many similar systems derived from other amphiphiles with laterally bulky hydrocarbon groups—for example, from the sodium and potassium salts of di(2-ethylhexyl)acetic acid or di(2-ethylhexyl)ethylsulphuric acid. Ekwall and associates have also observed this phase (their phase F) in certain ternary aqueous systems containing two n-alkyl amphiphiles, for example, sodium caprylate with decanol–1.⁽⁹⁾ The structure of the M_2 phase, like that of the M_1 phase, consists of parallel fibrous micelles in two-dimensional hexagonal array. In the M_2 phase however, it is the polar groups and aqueous region $\bar{W}$ that form the micellar cores while the hydrocarbon groups constitute a liquid continuum between these cores. Clearly in this phase, $R_x = 1$ along the fibres while $R_y > 1$ around them.

In the Aerosol OT/water system, the M_2 phase extends, at room temperature, from a concentration of about 84% up to the anhydrous salt. The anhydrous soaps of the metals of Group II of the Periodic Table, although crystalline at room temperature, apparently yield M_2 mesophases at elevated temperatures.⁽¹⁹⁾

The reason why fibrous M_2 mesophases are formed in these cases although, under comparable conditions, the alkali metal soaps of the n-alkanoic acids yield lamellar G mesophases, probably involves steric effects. With the straight-chain soaps the packing of the n-alkyl groups diverging around a system of fibrous or spherical polar cores, so as to form a liquid continuum between them, might well present difficulties in space filling. On the other hand, with Aerosol OT, accommodation of the highly branched and laterally bulky hydrocarbon groups around the fibrous polar cores would be an easier matter. With the soaps of the divalent metals the presence of two alkyl chains per metal ion would likewise facilitate space filling within a fibrous aggregate. Finally, space filling in the interfibre continuum of Ekwall's F phases, which contain two straight-chain amphiphiles, is probably permitted by the location of a considerable proportion of the less polar amphiphile outside the $\bar{C}$ layer and included within the interfibre continuum or $\bar{O}$ region. Evidence for such a distribution of amphiphile within the F phase in the sodium caprylate/decanol system has been advanced on the basis of X-ray diffraction studies.(9)

The M_2 phases of certain magnesium and cadmium soaps exist in two modifications,(19,1) stable at different temperatures. These two forms probably arise from a change in the mutual orientation of the polar groups with change in temperature. Analogous changes could arise with other fused mesophases. Indeed, as already noted, the transition from the lamellar neat soap phase to the lamellar soap boiler's neat phase, which occurs on dilution at high concentrations in the sodium laurate/water (Fig. 2) and other similar systems,(5) is probably of this type.

PHASES INTERMEDIATE BETWEEN THE M_1 AND G PHASES

It can be seen in Fig. 2 and Fig. 3 that both the M_1 and G phases show maxima in thermal stability at particular concentrations which, for convenience, we will term C_{M_1} and C_G respectively. At these concentrations the M_1 and G micellar structures respectively attain their greatest stabilities and are least readily disintegrated by thermal fluctuations. At concentrations somewhat above C_{M_1} ($R_x < 1$, $R_y = 1$) the fibrous micelles of the M_1 phase tend to undergo thermal breakdown in virtue of those thermal fluctuations which lead to loci of higher concentrations where R_x tends to become unity. At concentrations somewhat below C_{M_1} the M_1 micelles tend to breakdown in virtue of those fluctuations which lead to loci of lower concentration where R_y tends to fall below unity. Analogous considerations apply to thermal breakdown of the G phase on either side of C_G.

In proceeding in Fig. 2 along a line such as $X' Y'$, we encounter the phase sequence

$$S_1 \rightarrow (S_1 + M_1) \rightarrow M_1 \rightarrow (M_1 + S_1) \rightarrow S_1 \rightarrow (S_1 + G) \rightarrow G$$

The S_1 phase, as constituted between the compositions C_{M_1} and C_G, will contain locally both G and M_1 micellar loci in thermal equilibrium. This underlies the eutectic phenomena associated with the point P in Fig. 2. At temperatures below that corresponding to this point, the G and M_1 mesophases undergo direct transition on changes in bulk composition, without intermediate formation of the amorphous solution phases S_1. At higher temperatures, cooling of the S_1 phase, intermediate in composition between M_1 and G, leads, dependent on composition, to separation of either the G phase or the M_1 phase or, when S_1 has the eutectic composition P, of both.

Although the behaviour observed in the sodium laurate/water system is as just described, with certain other soaps cooling of a S_1 phase intermediate in composition between M_1 and G may lead to the separation of a number of individual mesophases intermediate in composition between M_1 and G. According to Luzzati and associates the following succession of " intermediate phases ", each named in accordance with its X-ray diffraction pattern, can arise in binary soap/water systems:(1,20) " deformed middle "; " rectangular "; " hexagonal complex "; " cubic ".

Not all of these phases are found in any particular soap/water system but, according to Luzzati, those which do arise always follow one another with increasing concentration in the order given. The experimental study of these intermediate phases is difficult since the range of composition of each individual phase is narrow, the systems are highly viscous and mixtures of the phases are frequently present. The credentials of certain of these phases may therefore be regarded as less certain than those of the M_1, G and M_2 phases just considered.(9) The cubic phase, or viscous isotropic phase, V_1, has however been observed by numerous workers in a variety of systems (cf. e.g., Fig. 4 and Fig. 5) and is fully authenticated. It was first characterized by Luzzati and associates as formed in aqueous systems containing the higher potassium soaps at temperatures in the region of 100 °C. It has also been studied at room temperature in binary aqueous systems containing potassium caprylate, sodium 2-ethylhexyl sulphate, *N*,*N*,*N*-trimethylaminododecanoimide and *N*,*N*-dimethyldodecylamine oxide. It has also been observed in ternary aqueous systems containing two amphiphiles, one more and one less polar.⁽⁹⁾ In these ternary systems a further intermediate phase, Ekwall's phase *C*, is often found intermediate between *G* (Ekwall's phase *D*) and M_1 (Ekwall's phase *E*).

Although X-ray diffraction measurements provide information concerning the arrangement and the repeating distances between the micellar units of the various intermediate phases, they do not establish the nature of the units themselves. A number of tentative micellar models for the individual intermediate phases have been suggested by several workers but these models have often later been revised or discarded. None can be considered as unequivocally established.

STRUCTURE OF THE V_1 PHASE

A number of structural models have been proposed for the well-defined V_1 phase. Chronologically, these include:

(i) spherical S_1 micelles arranged in a face centred cubic lattice within an aqueous continuum⁽²⁰,²¹⁾ (" Cubic I " structure);

(ii) inverse spherical S_2 micelles similarly arranged, the hydrocarbon chains forming a hydrocarbon continuum between the polar cores⁽²²⁾ (" Cubic II " structure); and, most recently,

(iii) a structure consisting of two interpenetrating networks composed of rods, each rod having the character of a short segment of an M_1 micellar fibre.⁽²³⁾ The interpenetrating networks crystallographically constitute a body-centred cubic structure (" Q_1 structure ").

Neither the " Cubic I " nor the " Cubic II " structure fits conformably between the M_1 and *G* structures. Moreover, a structure of the " Cubic I " type must apparently now be assigned to the recently characterized cubic phase S_{1c} which, as will shortly be discussed, occasionally arises between the S_1 and M_1 phases.

With regard to the Q_1 structure it is difficult to see what intermolecular forces could stabilize the postulated network in a system in which the $\bar{O}$, $\bar{C}$ and $\bar{W}$ regions are all fluid in character.

To the writer it seems that, somewhat as the M_1 and *G* phases arise on cooling the intermediate S_1 phase by homo-aggregation of either M_1 or G micellar units respectively, so the "intermediate mesophases" may arise by aggregation of both M_1 and G units jointly or of some type of hybrid unit.

Such hybrid aggregation might occur in various ways according to the relative abundance and extension of the M_1 and G units present. This would be expected to vary in a regular manner with concentration. The proposal of detailed hybrid structures for the successive individual intermediate phases must however await further studies.

It may be mentioned that, whereas the S_1 and V_1 phases show high resolution NMR spectra, the M_1, M_2 and G phases do not.(24,17) This may possibly be related to the presence of indefinitely extended micellar systems in the M_1, M_2 and G phases in contrast to the presence of smaller and more mobile units in the S_1 and V_1 phases. This seems in better accord with the idea of a hybrid structure for the V_1 phase than with the indefinitely extended Q_1 network model. NMR studies of other "intermediate phases" would be of much interest.

THE INVERSE CUBIC OR INVERSE VISCOUS ISOTROPIC PHASE V_2

A cubic phase, which is complementary to the V_1 phase, arises intermediate between the G and M_2 phases in the Aerosol OT/water system (Fig. 3) and in many other binary and ternary systems. This phase, which shows a high resolution NMR spectrum,(17) may possibly possess a hybrid structure derived jointly from M_2 and G units.

The V_2 phase is apparently to be identified with the cubic Q_2 phase observed by Spegt and Skoulios(19) in the case of the anhydrous fatty acid soaps of strontium and barium at high temperatures and with calcium ω-phenylundecanoate at room temperature. It was for these Q_2 phases that the interpenetrating network structure (here of inverse form) was first postulated by Luzzati and Spegt.(25) This interpretation was later extended to cover the Q_2 phase found in lecithin/water systems at high concentrations, and to the Q_1 phase observed in other systems of higher water content.(23,26,27)

THE HYDROPHILIC CUBIC PHASE S_{1_c}

Analogous to the formation of the M_1 and G phases by the mutual long-range ordering of M_1 and G micelles respectively, in certain circumstances mutual ordering of spherical S_1 micelles can apparently give rise to a mesophase in which these micelles are arranged in some form of cubic lattice. This phase was recorded by Fontell, Mandell and Ekwall(28) in the decaethyleneglycol monolaurylether/water system at room temperature at 40–44% concentration. It has recently also been characterized by Balmbra, Clunie and Goodman(8) in the dodecyltrimethylammonium chloride/water system (Fig. 5). It also occurs with the C_{10} and C_{14} but not with the C_{16} and C_{18} trimethylammonium chlorides nor with any of the corresponding bromides.

For the formation of a phase having the structure S_{1c} in a binary amphiphile/water system it is clear that the amphiphile must be constituted so that the replacement of the S_1 micelles with other forms, which normally occurs with increasing concentration, does not take place over a concentration range that is so low that the S_1 micelles never attain sufficient proximity for their mutual ordering. It would be expected that the asymmetry in the interfacial interaction of polar groups, which is believed to promote the formation of M_1 micelles, would, at a given concentration, be less with the $-N(CH_3)_3Cl$ group than with the more bulky $-N(CH_3)_3Br$ group. This view is supported by the X-ray diffraction studies of Reiss–Husson and Luzzati(18) who found evidence that while at 27 °C in the cetyl trimethylammonium bromide/water system conversion of spherical to fibrous micelles commences at a concentration of about 5%, with the corresponding chloride spherical micelles are still predominant even at a concentration of 40%. This type of difference probably accounts for the formation of the S_{1c} phase by the C_{10}, C_{12} and C_{14} trimethylammonium chlorides although not by the corresponding bromides. The non-formation of the S_{1c} phase by the C_{16} and C_{18} trimethylammonium chlorides is probably due to displacement of the $S_1 \rightarrow M_1$ interconversion process to lower concentrations on increase of molecular weight. At these lower concentrations the S_1 micelles are insufficiently close together for mutual long-range ordering to occur. It is of interest that the S_{1c} phase is produced on solution of hydrocarbon in S_1 solutions of sodium caprylate of suitable concentration although, in absence of hydrocarbon, increase in concentration (accompanied by reduction in area per polar group) leads to formation of the M_1 mesophase.(28) This is probably because solution of hydrocarbon increases the size and mutual proximity of the S_1 micelles without markedly affecting R or the area per polar group. Increase in concentration, on the other hand, produces a decrease in area per polar group and leads to the condition, $R_x < 1$; $R_y = 1$, which gives rise to formation of the M_1 phase.

IDEALIZED PHASE DIAGRAM INCLUDING THE AMORPHOUS SOLUTION PHASE AND THE SUCCESSION OF FUSED MESOMORPHOUS SOLUTION PHASES FORMED IN BINARY AMPHIPHILE/WATER SYSTEMS

An idealized phase diagram showing the relationships between the amorphous solution phase and the succession of fused mesomorphous solution phases found in binary amphiphile/water system is shown in Fig. 10. Of the "intermediate phases" only the V_1 and V_2 phases are included.

In this idealized diagram the ranges of existence of all the mesophases are drawn of similar extent, the peaks are represented as of equal heights and the eutectics of equal depth. In real systems, as already instanced by Figs. 2–5, not all the phases arise and the temperatures of the peaks and eutectics vary widely. Nonetheless, in real systems those phases that do appear apparently always follow the sequence shown with increasing concentration. With amphiphiles of analogous constitution a particular peak tends to arise at a lower concentration the higher the molecular weight of the amphiphile (cf. Method Ic of Table 1 below).

In the sequence of phases illustrated in Fig. 10 the effect of increasing concentration can reasonably be assigned to its tendency to increase R and thus regularly to affect micellar conformation. The effect of increasing temperature can be interpreted mainly in terms of the effect of increased thermal motion in increasing fluctuations in micellar form and in tending to break down long-range order. Although the influence of increasing temperature on the ratio R is usually small it may in some specific cases be either to increase or to decrease R. In these cases, in addition to the general disintegrating effect just noted, the various peaks in Fig. 10 will tend to be bent towards the left or right respectively. The former effect is evident in Figs. 4 and 5.

TABLE 1 General methods for influencing phase equilibria by variation of $\bar{R}$ in amphiphile solutions containing an organic liquid O_1, an amphiphilic salt C_1 and water W_1

Note: R increases with $A_{\overline{CO}}/A_{\overline{CW}}$, i.e. with $\left[(A_{H_{\overline{CO}}} + A_{L_{\overline{CO}}})/(A_{H_{\overline{CW}}} + A_{L_{\overline{CW}}})\right]$

Method classification	Details of method	Influence on R	Probable mechanism of influence on R	Effect on the phase ratio in an initially heterogeneous system containing any two in the following succession of phases: $O_1^{x}, S_1, S_{1_C}, M_1, V_1, G, V_2, M_2, S_2, W_1^{x}$
Ia	Reduction in the relative proportion of W_1	R tends to be increased	$A_{\overline{CW}}$ diminished by mass action	Increase in proportion of the right-hand phase present Where a single-phase system is initially involved, the progressive application of a particular method will finally tend to the precipitation from this phase of the neighbouring successional phase. With particular systems certain phases of the sequence do not appear, but the general order of succession with variation in R remains the same. Superimposed on the directional effects of methods Id and IIb is the general tendency of $\bar{W}$-soluble materials to inhibit the formation of liquid crystalline solutions
Ib	The addition to O_1 of an oil-soluble compound of more polar (hydrophilic) character than O_1. Alternatively, this may be regarded as the addition to C_1 of an amphiphilic compound less polar than C_1	R tends to be increased	Reduction of $A_{H_{\overline{CW}}}$ by incorporation of amphiphilic additive in $\bar{C}$ layer and/or increase of $A_{H_{\overline{CO}}}$	
Ic	Increase in the relative lipophilic character of C_1, e.g., by increase of molecular weight, substitution of an organic for an inorganic counter-ion, or by certain changes in constitution(10)	R tends to be increased	$A_{L_{\overline{CO}}}$ increased and/or $A_{H_{\overline{CW}}}$ diminished	
Id	The addition to W_1 of an inorganic salt	R tends to be increased	$A_{H_{\overline{CW}}}$ diminished	
IIa	Reduction in the relative proportion of O_1	R tends to be decreased	$A_{\overline{CO}}$ diminished by mass action	Increase in proportion of the left-hand phase present
IIb	The addition to W_1 of a water-soluble organic liquid of more lipophilic character	R tends to be decreased	$A_{L_{\overline{CW}}}$ increased	
IIc	Increase in the relative hydrophilic character of C_1, i.e., method Ic in reverse	R tends to be decreased	$A_{H_{\overline{CW}}}$ increased and/or $A_{L_{\overline{CO}}}$ diminished	
IId	The addition to O_1 of a less hydrophilic oil-soluble component, e.g., medicinal oil	R tends to be decreased	Reverse of mechanism of method Ib	

O_1^{x}, W_1^{x} Excess non-solubilized organic or aqueous phase if present. If no organic liquid has been added O_1 must be taken to indicate the hydrocarbon region of the micellar system.

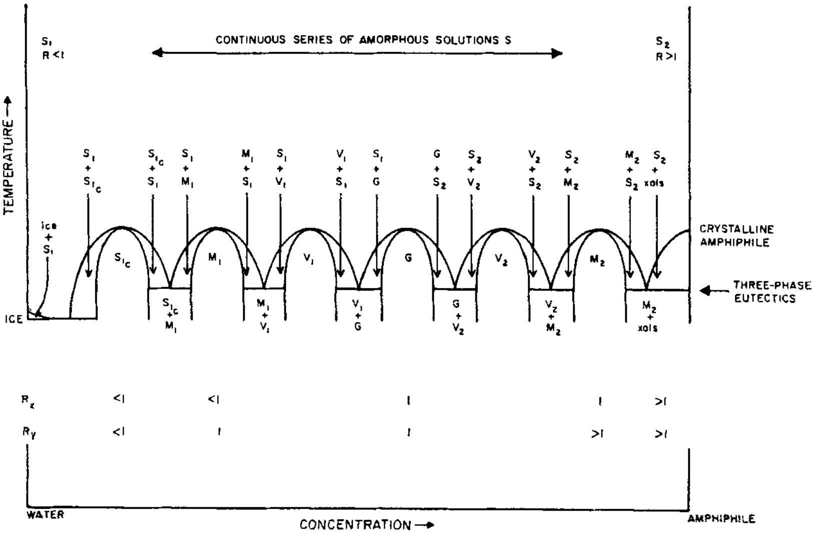


Figure 10. Idealized phase diagram including the amorphous solution phase $S(S_1, S_2)$ and the succession of fused mesomorphous solution phases realizable in binary amphiphile/water systems. In individual real systems not all the phases arise, but those that do succeed one another with increasing concentration in the order indicated; further the heights of the different peaks and the depths of the eutectics vary greatly.

Diagrammatic Representation of Intermicellar Equilibria and Associated Phase Changes

The generalizations of Fig. 10 are also expressed in Fig. 11 in which, again, micellar form is correlated with the ratio R.

Within the individual mesophases (with the possible exception of the " intermediate phases ", V_1, V_2, etc.) the micellar form is characteristic and uniform and there is long-range intermicellar order.

Within the amorphous solution phase S there is an equilibrium of thermally fluctuating micellar forms. If, within the S phase, under particular conditions of composition and temperature, a particular micellar form attains a sufficient concentration and extension, then micellar interaction leads to mutual ordering of the micelles and to the separation of the corresponding homo-mesophase (S_{1c}, M_1, G, M_2). Further, it appears possible that under certain conditions there may be micellar interactions involving more than one micellar type that

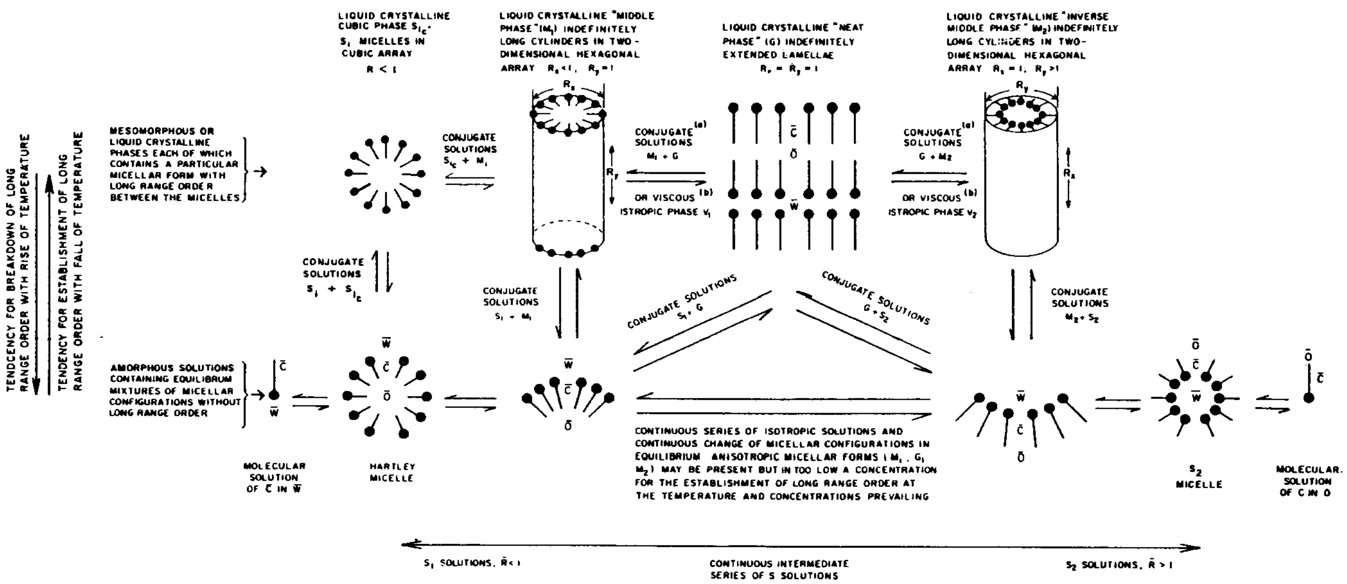


Figure 11. Correlation between the ratio R and the micellar form in the fused amorphous and mesomorphous phases produced in amphiphilic systems.

lead to the separation of hybrid mesophases (V_1, V_2 and other " intermediate " mesophases).

Mesophase Formation in Multicomponent Systems

In the remainder of this article a brief account will be given of mesophase formation in multicomponent amphiphilic systems.

Systems Containing Water, Hydrocarbon and Two Amphiphiles, One Hydrocarbon-soluble and One Water-soluble

Many systems of this type, often including additional components, were examined by the writer in a study initially concerned with the formulation of storage-stable emulsifiable concentrates.(10)

From the point of view of this technical objective both crystal and liquid crystal formation are usually undesirable. In the systems examined branched-chain salts were mainly used, because, in comparison with the *n*-alkyl compounds, they crystallize much less readily and are less inclined to give highly viscous and technically intractible liquid crystalline solutions. Indeed, in the particular systems examined, of all the mesophases included in Fig. 10, only the comparatively non-viscous lamellar liquid crystalline phase G was encountered. This fortunately considerably simplified these early phenomenological and orientative studies. It was to correlate and interpret the observations made in this work that the R-theory(10,11) was first developed. Since the only micellar phases encountered were the amorphous solution phase $S(S_1, S_2)$ and the lamellar liquid crystalline phase G, only the possibilities $R < 1$, $R = 1$ and $R > 1$ were envisaged. The possibility of dissymmetry in R, for example $R_x < 1$, $R_y = 1$ as in the M_1 phase, did not at that time suggest itself.

As a typical example of the approach adopted, the behaviour observed when octanol–1 is gradually added to a mixture of equal volumes (10 ml total) of an aqueous solution of undecane–3 sodium sulphate (20%w) and an aromatic-free hydrocarbon fraction (b.p. 188–213 °C) will be discussed. The observed sequence of phase changes, which are readily reversible with changes in composition or temperature, is illustrated by Fig. 12, (1)–(8).

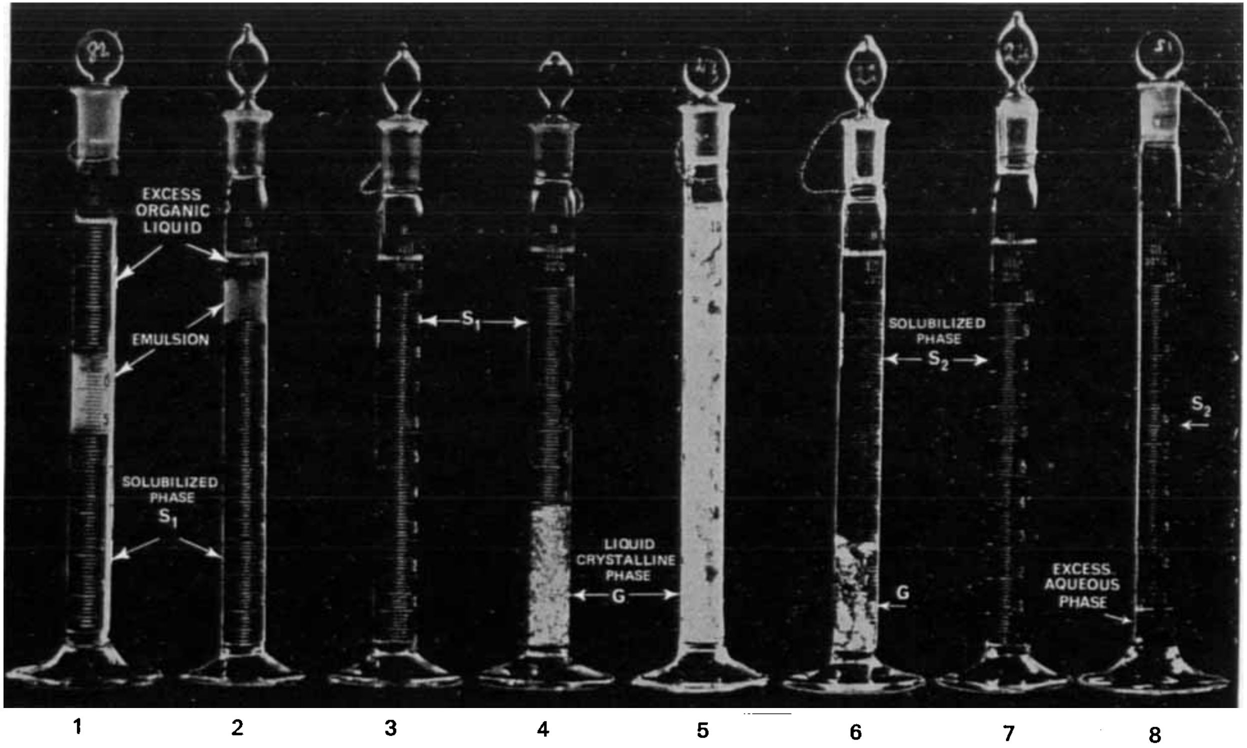


Figure 12. Accompanying phase changes at 20 °C on adding octanol–1 to a mixture of undecane–3 sodium sulphate solution (5 ml, 20w%) with aromatic-free hydrccarbon (5 ml); systems photographed between crossed polaroid sheets. Note that S_1 and S_2 solutions are clear and the persistent orientation in certain regions of G phases.

(1) No octanol added, (S_1 + excess hydrocarbon phase)
(2) 0.85 ml octanol–1 added
(3) 0.91 ml octanol–1 added, S_1 (isotropic)
(4) 1.00 ml octanol–1 added, $S_1 + G$
(5) 1.20 ml octanol–1 added, G (birefringent)
(6) 1.38 ml octanol–1 added, $G + S_2$
(7) 1.70 ml octanol–1 added, S_2 (isotropic)
(8) 2.13 ml octanol–1 added, S_2 + excess aqueous phase

In (1) the undecane–3 sodium sulphate is dissolved in the aqueous phase mainly as spherical S_1 micelles (Hartley micelles). Solution (or " solubilization ") of hydrocarbon in the micellar interior, which necessarily involves reduction in the curvature of the $\bar{C}$ monolayer, is strictly limited by the condition, $R < 1$.

In (2) the added octanol, although distributed between the excess hydrocarbon and the $\bar{W}$, $\bar{O}$ and $\bar{C}$ regions of the aqueous amphiphile phase so as to be of uniform activity throughout, principally enters the S_1 micelles between the alkyl sulphate molecules, C_8 hydrocarbon groups beside C_{11} hydrocarbon groups and $-OH$ groups beside $-SO_4Na$ groups. The highly polar $—SO_4Na$ groups are thus diluted at the interface by the less polar $—OH$ groups. $A_{\bar{C}\bar{W}}(=A_{H\bar{C}\bar{W}}+A_{L\bar{C}\bar{W}})$ is thus diminished by reduction in $A_{H\bar{C}\bar{W}}$ and the value of $A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}$ and hence of the ratio R is thus increased. This permits reduction in curvature of the micellar surface so that further hydrocarbon can enter the micellar interior.

In (3) the continuation of these processes results in complete solution of the hydrocarbon in the amorphous solution phase S_1.

In (4), with further addition of octanol–1 the processes envisaged under (2) and (3) reach a stage where thermal fluctuations establish an equilibrium between the two conjugate phases S_1, in which R is statistically less than unity, and G in which $R = 1$. The character of the equilibrium between the S_1 and G phases has already been discussed for the case of the sodium laurate/water system (p. 153).

In (5), on further addition of octanol–1, unit value of R is established throughout the system which now constitutes a single lamellar liquid crystalline solution phase G.

In (6) further addition of octanol–1 tends to produce the condition $R > 1$ and thermal fluctuations establish an equilibrium between two conjugate phases, the amorphous solution phase S_2, in which R is statistically greater than unity, and the residual G phase ($R = 1$).

In (7) further addition of octanol results in complete conversion of the system to the amorphous solution phase $S_2(R > 1)$.

In (8) continuing increase in R results in extrusion of an excess aqueous phase from the micellar interior. This is complementary to the extrusion of an excess hydrocarbon phase on reduction of R on following the reverse sequence, (3) to (2), that is $S_1 \rightarrow (S_1 + \text{excess}$ hydrocarbon phase).

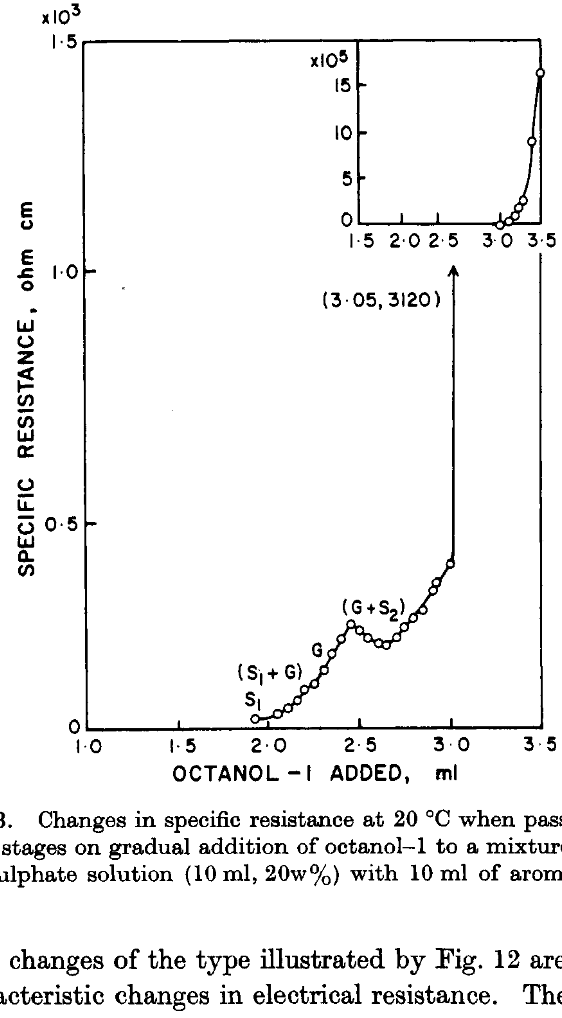


Figure 13. Changes in specific resistance at 20 °C when passing through S_1, G and S_2 stages on gradual addition of octanol–1 to a mixture of undecane–3 sodium sulphate solution (10 ml, 20w%) with 10 ml of aromatic-free hydrocarbon.

Phase changes of the type illustrated by Fig. 12 are accompanied by characteristic changes in electrical resistance. These are shown, for the system of Fig. 12, in Fig. 13. The curves for both the S_1 and S_2 branches of the S phase show a continuous increase in electrical resistance as R is increased and the thermally fluctuating micellar system progressively tends from $\overline{W}$-continuity towards $\bar{O}$-continuity. Further, the S_1 and S_2 branches appear to form parts of a single curve which is interrupted by the interposition of the G phase. The resistance of the G phase itself is higher than that of either the S_1 or S_2 phases of neighbouring composition. This is probably because a crystallographic unit of the G phase, although both $\bar{O}$-continuous and $\overline{W}$-continuous in a plane normal to its optic axis, is both $\bar{O}$-discontinuous and $\overline{W}$-discontinuous in all other planes. Under conditions of temperature or composition where a G phase is not interposed, the continuous transition $S_1 \rightarrow S_2$ is accompanied by a continuous increase in electrical resistance (cf. Fig. 15 on p .174).

INFLUENCE OF A VARIETY OF COMPOSITIONAL CHANGES ON THE RATIO R

By noting the effect of stepwise modification in the composition or temperature of series of systems similar to that illustrated by Figs. 12 and 13 on the amounts of hydrocarbon-soluble amphiphile required

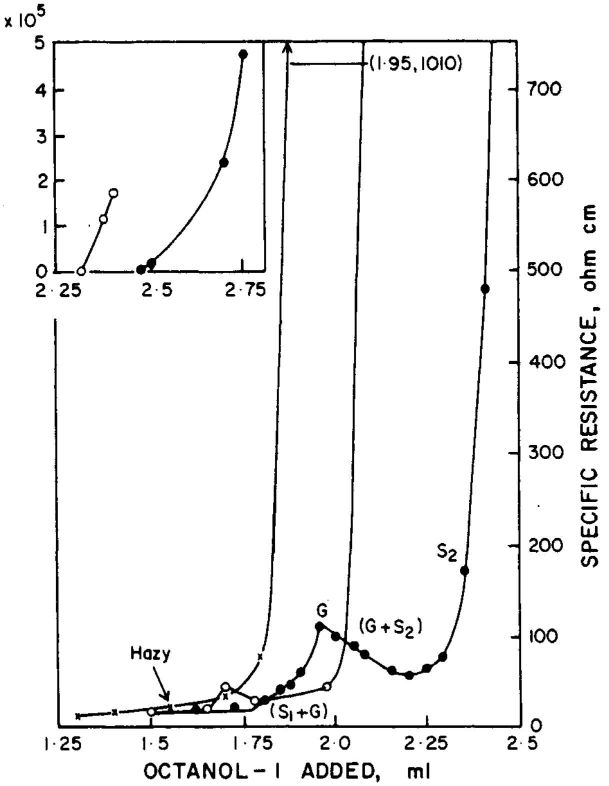


Figure 14. Changes in specific resistance at 20 °C when passing through S_1, G and S_2 stages on gradual addition of octanol-1 to a mixture of undecane-3 sodium sulphate solution (10 ml, 20w%) containing sodium sulphate: ●0.1 g, or ○0.2 g, or ×0.4 g) with 10 ml of aromatic-free hydrocarbon.

to reach corresponding stages in the phase progression, the qualitative influence of the modification on the ratio R may be inferred. For example it can be seen from Fig. 14 that corresponding points on the curves of resistance against octanol-1 addition are displaced to lower octanol contents by progressive addition of sodium sulphate. It may be inferred that addition of sodium sulphate increases the ratio R.

As a result of many experiments on these lines a table correlating the effects of various types of compositional change on the ratio R and on the formation of the S_1, G and S_2 phases was compiled. This compilation as extended, to some extent tentatively, to cover systems in which the additional mesophases of Fig. 10 are produced, is given in Table 1. Space does not permit its detailed discussion. The following points may be noted:

(1) The table as originally compiled applied to systems in which the more hydrophilic amphiphile was ionic. The same behaviour is broadly followed if this amphiphile is a polyethanoxy compound. The effect of added water-soluble lower alkanols is however reversed (cf. Method IIb). This is probably because, with the polyethanoxy amphiphile, the water-soluble organic compound is distributed in favour of the polyethanoxy zone of the $\bar{C}$ layer, whereas with the ionic amphiphiles it predominantly enters the $\bar{W}$ region.(11)

(2) The effect of inorganic salts on amphiphilic phases has mainly been investigated in systems in which only the S_1, G and S_2 phases arise.(10) In this case the effect of added sodium sulphate is both to increase R and to decrease the range of compositions forming the G phase at a given temperature. Both effects are evident in Fig. 14. Other additives which enter the $\bar{W}$ region, also restrict the range of the G phase independently of whether they increase or decrease R. The effect is probably associated with interruption of water-to-water and water-to-amphiphile hydrogen bonding.

The effect of inorganic salts on the stability of other amphiphilic mesophases needs further study. The effects on the formation of the " intermediate " phases might prove particularly interesting. In certain 1-monoglyceride/water systems Krog and Larsson have found that the V phase (whether of V_1 or V_2 character seems uncertain(9,11)) is stabilized relative to the G phase by sodium chloride.(29)

(3) Independently of its general effect in promoting thermal fluctuations and the breakdown of long-range order, increase in

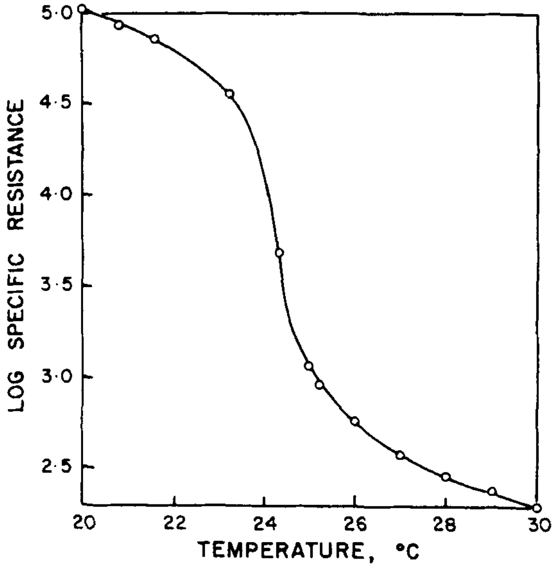


Figure 15. Changes in specific resistance with change of temperature of a solution containing aromatic-free hydrocarbon (10 ml), octanol–1 (2.25 ml), undecane–3 sodium sulphate solution (10 ml, 20w%) and sodium sulphate (0.2 g).

temperature may either increase or decrease R. In the systems in which the amphiphile is mainly non-ionic, increase of temperature usually increases R (Fig. 4) probably by reducing $A_{H\bar{C}\bar{W}}$ through dissociation of hydrogen bonds. With ionic amphiphiles a reduction in R with rising temperature is sometimes found. A striking result of this effect is provided by the electrical resistance changes illustrated by Fig. 15. In this system rise of temperature, by decreasing R, produces a continuous transition within the S phase from S_2 to S_1; that is a thermally fluctuating amorphous micellar system which is predominantly $\bar{O}$-continuous (S_2) is progressively transformed into one that is predominantly $\bar{W}$-continuous (S_1). Although in Fig. 15 the change $S_2 \rightarrow S_1$ is continuous and involves no change of phase, with certain other similar systems intermediate separation of the G phase occurs with rising temperature,⁽¹⁰⁾ i.e., $S_2 \rightarrow (S_2 + G) \rightarrow G \rightarrow (G + S_1) \rightarrow S_1$.

TERNARY AQUEOUS SYSTEMS

A number of ternary systems have been carefully investigated,

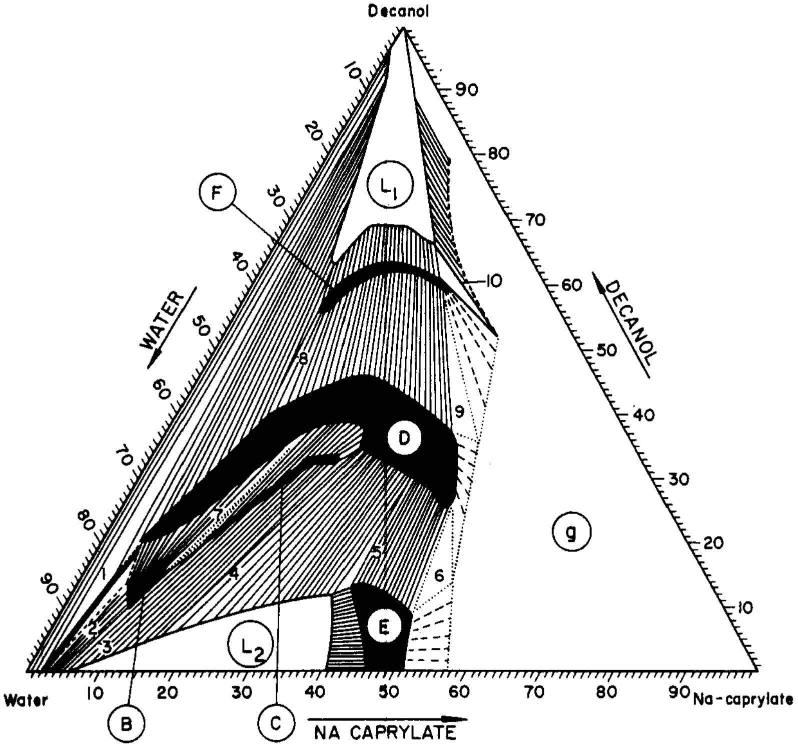


Figure 16. Phase diagram for the three-component system sodium caprylate/decanol/water at 20 °C. The concentrations are % by weight.(9)

L_1–Homogeneous isotropic solutions in water.

L_2–Homogeneous isotropic solutions in decanol.

B, C, D, E, F–Homogeneous mesomorphous phases.

g–Solid crystalline sodium caprylate and hydrated sodium caprylate with fibre structure.

1–10–Three-phase triangles.

Note In the system of nomenclature used in the present paper:

$L_1 = S_1$
$L_2 = S_2$
$D = G$; $B =$ a second form of G
$C =$ an intermediate phase
$E = M_1$
$F = M_2$

particularly by Ekwall and associates.(9) Results have usually been represented on triangular isothermal phase diagrams.

The phase equilibria in the most intensively studied system are illustrated in Fig. 16. Many other systems of this type containing two amphiphiles, one relatively hydrophilic (A_1) and the other relatively lipophilic (A_2) have also been investigated. They give phase diagrams broadly similar to Fig. 16. All of the phases indicated in Fig. 10 are represented in one or other of these systems.

In such diagrams, phase sequences encountered with changes in composition directed along lines such as *WP* in Fig. 17 can be regarded as following the application of Method Ia of Table 1 to an amphiphile of composition *P*. Except in zones where conjugate phases occur, *P* is found to behave much as a single amphiphile of polarity inter-

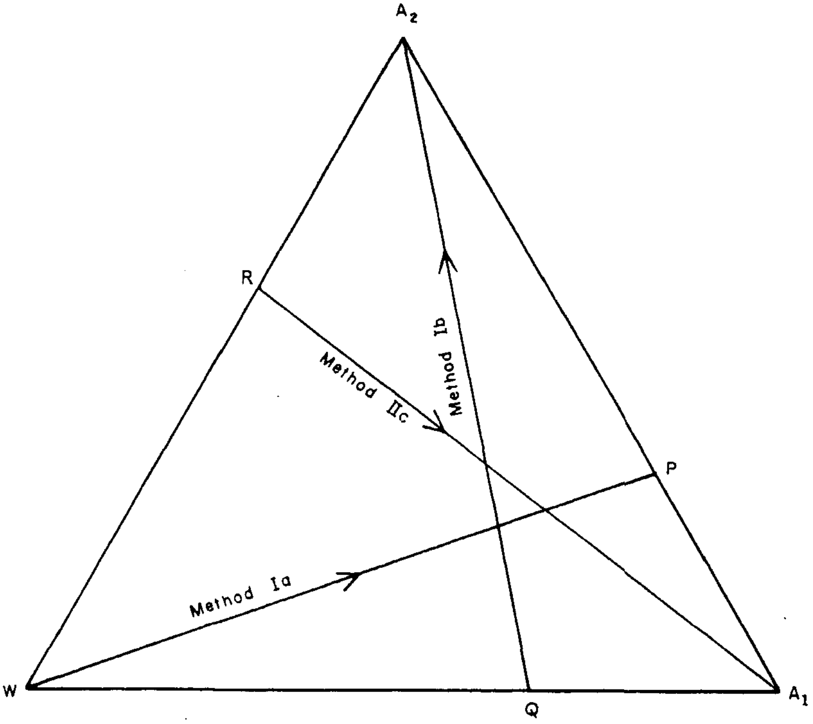


Figure 17. Composition changes following Methods 1a and 1b of Table 1 in a ternary aqueous system containing two amphiphiles, one relatively hydrophilic (A_1) and the other relatively lipophilic (A_2).

mediate between A_1 and A_2. However, as already noted in discussing the formation of the M_2 phase in these systems, there will be appreciable fractionation of A_1 and A_2 between the $\bar{C}$, $\bar{O}$ and $\bar{W}$ zones within the individual phases. Where conjugate phases occur, macroscopic fractionation of P takes place, A_1 being distributed in favour of the phase richer in water.

Phase sequences encountered with changes in composition directed along lines such as QA_2 and RA_1 may be regarded as following the application of Methods Ib and IIc respectively of Table 1.

When Ekwall's phase diagrams, which have recently been collected and discussed,(9) are examined from this point of view they are found, apparently without exception, to be in good accord with Table 1 and with the generalizations suggested in Figs. 10 and 11.

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